# SEQUENCE DISTRIBUTION STUDIES OF DICHLOROPROTOANEMONIN - METHYL METHACRYLATE COPOLYMERS

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Polymerization of 1,3-diene type monomers to give polymer units which spontaneously undergo an elimination reaction is a convenient means for preparing polymers having a high degree of conjugated unsaturation in the main chain. Dichloroprotoanemonin (DCPA) (I) is an excellent example of such a monomer as it readily forms 1,4-addition copolymers with methyl methacrylate, styrene, etc., and under suitable conditions undergoes a rapid dehydrohalogenation to give conjugated DCPA residues.[1] The various possible addition and elimination reactions are shown in scheme A.

Scheme A:
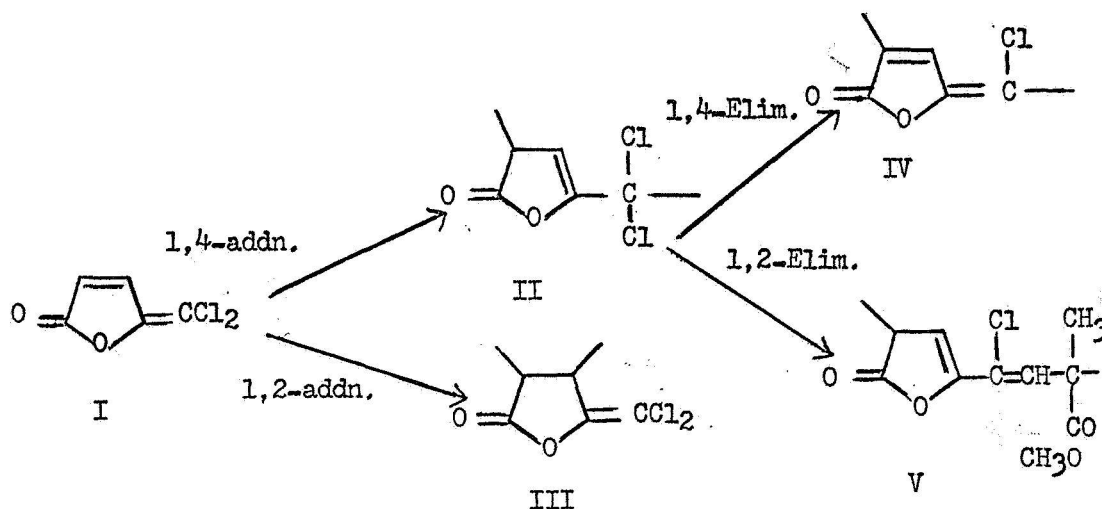
We reported earlier[2] that the DCPA residues consist almost entirely of structures IV and V. Structures II and III are ruled out on the basis that one equivalent of HCl is eliminated per equivalent of DCPA that enters the copolymer. The presence of structure IV from 1,4-elimination is confirmed by infrared absorption at 1770 cm^{-1} for the conjugated lactone carbonyl group, and by ultraviolet absorption at λmax 300 mμ for the three double bond conjugated system. An additional infrared bond at 1800 cm^{-1} is consistent with the non-conjugated carbonyl group, and suggests the presence of structure V from 1,2-elimination of hydrogen chloride.

Several additional DCPA-MMA copolymers were prepared for the purpose of confirming the previous results on chloride elimination and for further spectral studies. These copolymerizations, Nos. 3, 4, 5 are reported in Table 1 and compared with the previously reported data for Nos. 1 and 2. The good agreement between the amount of chloride eliminated as HCl and the amount remaining in the copolymer confirms the previous observation that half of the chloride is eliminated on copolymerization of DCPA with methyl methacrylate. The slightly high values for the percent chloride eliminated may be attributed to errors introduced by the inability to isolate completely all of the copolymers formed.

Ultraviolet spectral studies have revealed that DCPA-MMA copolymers possess, in addition to the intense band at 300 mμ, a weak band at 368 mμ, Figure 1. Whereas the band at 300 mμ is readily attributable to the three double bond conjugated system of structure IV, the band at 368 mμ indicates that more extended conjugated structures may be present. These structures

are very possibly DCPA residue diads (VI) which, having a six double bond conjugated system, would be expected to absorb at about the observed position.
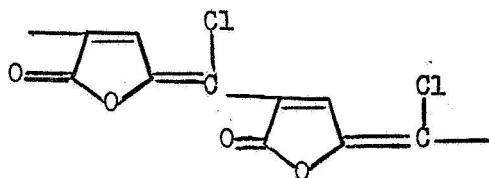
VI

If this is the case, the absorption band at 368 mμ, being well resolved from the 300 mμ band, would provide a means for measuring the diad sequence distribution in this system.

In the case of DCPA-styrene copolymers, distinct absorption peaks above 300 mμ are completely lacking, Figure 2. Since copolymers of styrene with cyclic monomers are usually highly alternating, the probability for diad formation in such cases is relatively low and, hence, the absence of a band at about 368 mμ for the DCPA-styrene copolymers supports the proposal that this band is due to DCPA residue diad sequences.

The absorbance at λ max 368 mμ was measured for the various copolymers, and since Beer's law held over the concentration range involved, the values were converted to absorbance for 0.1% solutions, Table 2. A plot of these values against copolymer composition, Figure 3, shows that the absorbance consistently increases with each increase in the DCPA residue in the copolymer. This result is compatable with the increasing probability of diad formation with increasing DCPA content. A plot of the absorbance at 368 mμ against the actual diad concentration should give a straight line if the diads were really responsible for this band.

However, in order to prepare this plot, the number distribution function[3] for diad formation had to be determined from the reactivity ratios. The data for the calculation of the reactivity ratios are reported in Table 3 and the feed copolymer compositions are plotted in Figure 4. Solution of the copylmer equation by the Fineman-Ross,[4] Mayo-Lewis,[5] and curve fitting methods provided the reactivity ratios listed in Table 4. The average value was used in the calculation of the copolymer composition curve, Figure 4, and the number distribution function, Table 5. In the calculation of the number distribution function the feed composition responsible for each of the copolymers was required. However, the feeds actually employed in the copolymerization reactions were unsatisfactory for this purpose because the constant passage of nitrogen through the system for HCl removal caused appreciable amounts of both monomers to be volatilized, thus changing the feed composition. For this reason the effective feed compositions which would have provided the various copolymer compositions obtained, were calculated from the copolymer compositions by means of the reactivity ratios. From the effective feed compositions and the reactivity ratios, the number distribution functions and finally the DCPA diad concentrations were calculated, Table 5.

A plot of the diad concentration against the absorbance is shown in Figure 5. The reasonably straight line produced supports well the original proposal that the band at λ max 368 mμ is due to diads sequences of DCPA residues in the copolymer. This particular system is one of the few cases where the quantity used for the measurement of the sequence is clearly resolved from that of the isolated unit.

A similar treatment of the 300 mμ band of the isolated DCPA conjugated unit, structure IV, has not yet afforded consistent results. However, since the distribution between 1,4- and 1,2-elimination to give structures IV and V is not known at present, accurate concentration values of structure IV cannot be determined. Also, the contribution of the diad to the absorbance at 300 mμ is not known, although at the low diad concentrations this factor is probably negligable.

EXPERIMENTAL

Dichloroprotoanemonin was prepared through the reaction of sodium trichloracetate with succinic anhydride according to the method of Winston and Sharp.[6] The white crystalline compound was purified by sublimation at 95°C (1 mm), mp 97.5°C. Elemental analyses were performed by Gailbraith Laboratories, Knoxville, Tennessee. Ultraviolet spectra were recorded on the Bausch and Lomb Spectronic 505 using 1.0 cm. cells (dioxane solutions).

Copolymerization Procedure

The copolymerizations were carried out in a three neck flask fitted with a reflux condenser and a gas inlet tube extending to the bottom of the flask. To the reflux condenser was connected a tube leading to a trap containing a known volume of standard sodium hydroxide solution. During the polymerization, nitrogen gas, dried by a previous passage through concentrated sulfuric acid, was introduced through the inlet tube in order to sweep the hydrogen chloride into the standard base solution. At the termination of the polymerization, the excess base was titrated with standard hydrochloric acid. The temperature of polymerization was held at 65° by a constant temperature bath. Addition of methanol to the reaction mixture, caused the polymers to precipitate. The polymers were pruified by three precipitations from acetone-methanol and were dried under reduced pressure for two days. Examination of the NMR spectra of the copolymers indicated that they were free of DCPA and solvent impurities. The copolymerization and elimination data are reported in Table 1.

Determination of Reactivity Ratios

Solutions of DCPA and methyl methacrylate in benzene were polymerized at 65° in sealed tubes. During the polymerization time of from 4-6 hrs. the color of the reaction mixture changed from colorless to golden-orange. Copolymers formed from the 0.05-0.4 mole fraction DCPA feeds were precipitated from methanol. Since copolymers from above 0.40 mole fraction DCPA feeds failed to precipitate on addition of methanol, the unreacted residual methyl methacrylate and solvents were evaporated on a rotary evaporator at room temperature. The residual lactone monomer was sublimed out of the polymer at 95°/1 mm. The residue was then dissolved in a small amount of benzene and reprecipitated from ligroin. The polymers were collected, washed, and dried under reduced pressure. The copolymers were then analyzed for chlorine and the copolymer compositions were calculated on the basis of one chlorine per DCPA residue, Table 3.

ACKNOWLEDGMENT

REFERENCES

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2. A. Winston and D. A. Chapman, Preprints of the IUPAC International Symposium on Macromolecular Chemistry, Brussels-Louvain, June 12-16, 1967, No. 1/6; J. Polymer Sci., in press.

3. G. Goldfinger and T. Kane, J. Polymer Sci., 3, 462 (1948).

4. M. Fineman and S. D. Ross, J. Polymer Sci., 5, 259 (1950).

5. F. R. Mayo and F. M. Lewis, J. Am. Chem. Soc., 66, 1594 (1944).

6. A. Winston and J. C. Sharp, J. Am. Chem. Soc., 88, 4196 (1966).

Table 1

Copolymerization of Dichloroprotoanemonin (M_1) with Methyl Methacrylate (M_2)

Copolymer No.	1	2	3	4	5
Mole Fract. M_1 in Feed	0.20	0.20	0.20	0.20	0.40
Wt. Feed (g)	5.65	5.65	5.65	5.65	6.28
Vol. Benzene (ml)	0	5	0	0	15
React Time (hr)	6.0	6.5	1.7	6.5	18
Wt. Copolymer (g)	1.33	2.23	1.22	-	0.505
Cl in Copolymer (%)	3.27	2.96	1.60	1.86	6.76
Total Cl in Copolymer (g)	0.043	0.066	0.020	-	0.0341
Total Cl Eliminated (g)	0.049	0.076	0.025	-	0.0350
Cl Eliminated (%)	53.3	53.5	55.6	-	50.5
DCPA in Copolymer (%)	11.8	10.7	5.8	6.74	24.4
Mole Fract. DCPA in Copolymer	0.094	0.086	0.036	0.053	0.202

Table 2

Ultraviolet Absorption Data for DCPA-MMA Copolymers at 368 mμ. in Dioxane

Copolymer No.	1	2	3	4	5
Copolymer Conc. (g/l)	1.096	1.550	1.630	1.912	0.916
Absorbance at 368 mμ	0.421	0.451	0.155	0.245	1.358
Absorbance (adjusted to 0.100% soln.)	0.384	0.291	0.095	0.128	1.48

Table 3

Feed Copolymer Composition Data for the
DCPA (M_1)-MMA ((M_2) System

Mole Fract. DCPA in feed f_1	Conversion %	Cl Anal., %	Mole fract. DCPA in Copolymer[a] F_1
0.05	41.7	1.97	0.06
0.1	35.2	2.97	0.08
0.2	12.1	4.55	0.13
0.3	2.4	6.84	0.20
0.4	3.3	7.74	0.23
0.5	7.1	10.53	0.32
0.6	11.4	11.51	0.36
0.7	2.7	18.19	0.60
0.8	2.9	15.85	0.51
0.9	4.2	20.50	0.69

a. Calculated on the basis of one chlorine per DCPA residue.

Table 4

Reactivity Ratios for
DCPA (M_1) - MMA (M_2) copolymerization

Method	r_1	r_2
Fineman-Ross	1.44	0.21
Mayo-Lewis	1.45 ± 0.45	0.16 ± 0.15
Curve Fitting	1.42	0.115
Average	1.43 ± 0.45	0.16 ± 0.15

Table 5

Calculation of the Diad Concentration of the
DCPA - MMA Copolymers

Copolymer No.	1	2	3	4	5
Copolymer Composition (Mole Fract. DCPA)	0.094	0.086	0.036	0.053	0.202
Feed Composition (Mole Fract. DCPA)[a]	0.139	0.126	0.052	0.077	0.305
Number Distribution Function for DCPA Diads (N)	0.0243	0.0220	0.0086	0.0131	0.0612
Diad Conc. (%)	0.144	0.118	0.0250	0.0442	0.745

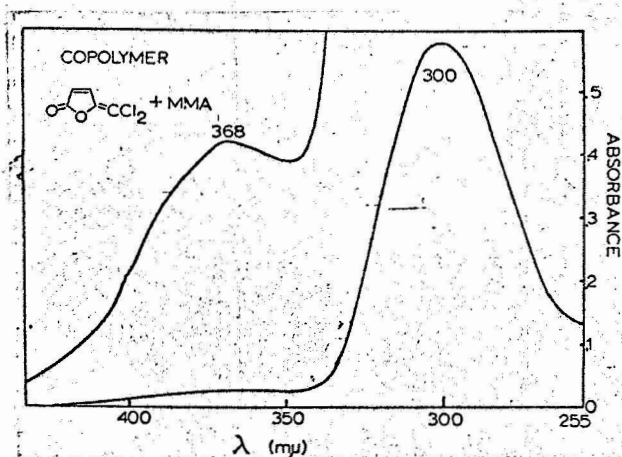a. Effective feed composition as calculated from the copolymer composition and the reactivity ratios.

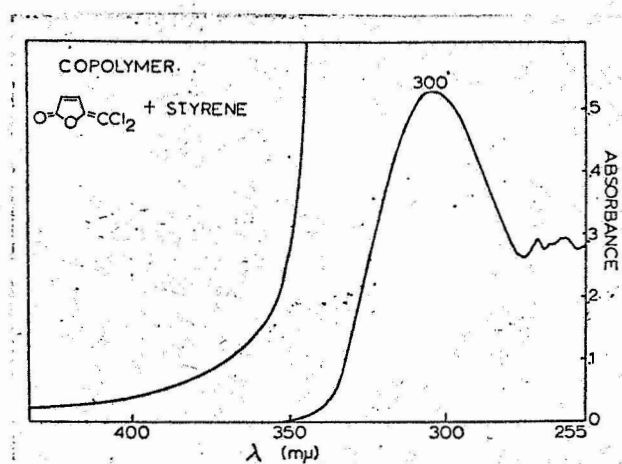Fig. 1. Ultraviolet spectrum of DCPA_MMA copolymer.

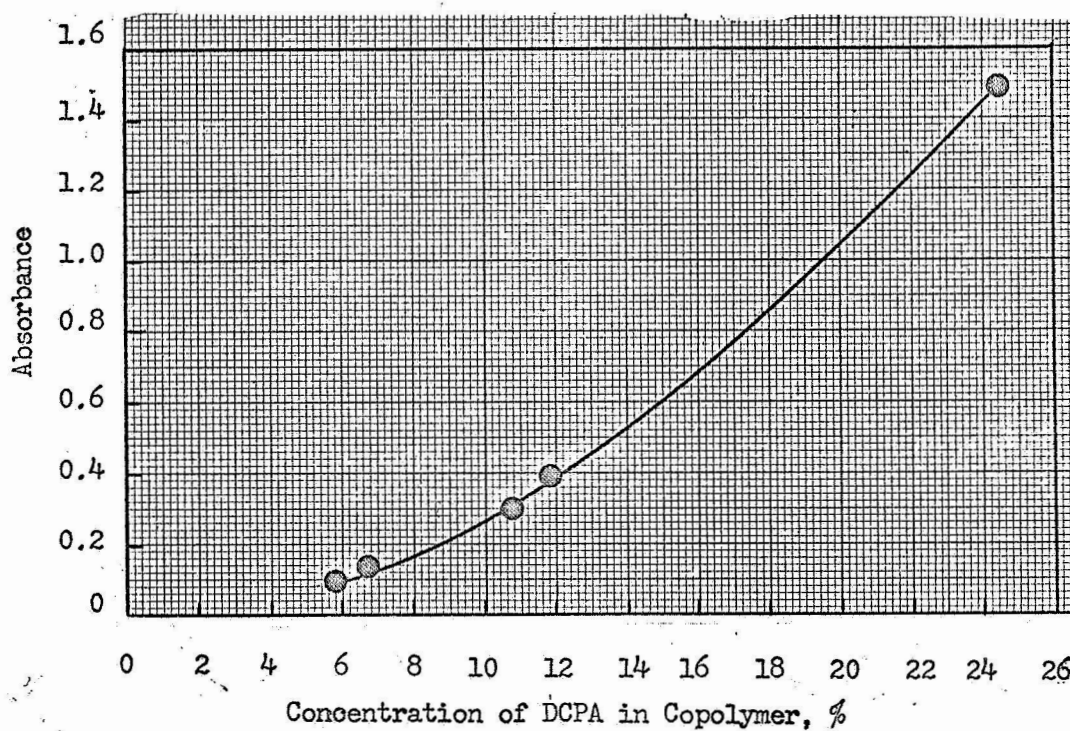Fig. 2. Ultraviolet spectrum of DCPA_Styrene copolymer.

Fig. 3. Relation between the concentration of DCPA residues in the copolymer and the absorbance at 368 mμ for 0.1% solutions.

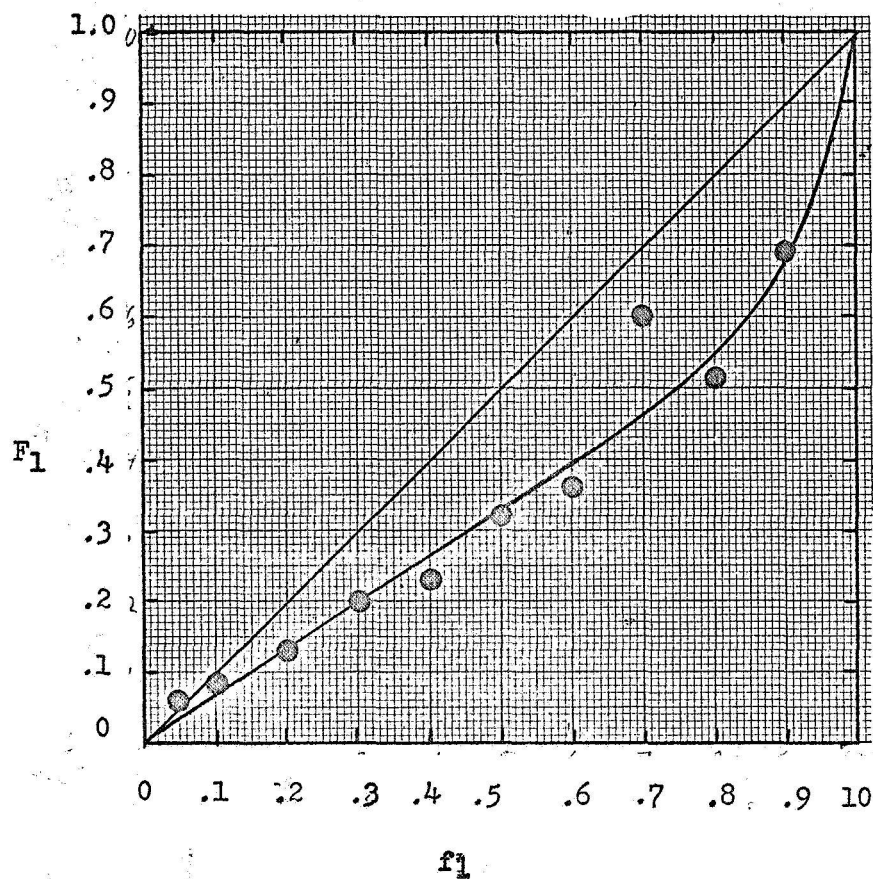Fig. 4. Feed-copolymer composition plot for DCPA
(M$_1$) - MMA (M$_2$). The curve is drawn for r_1 =
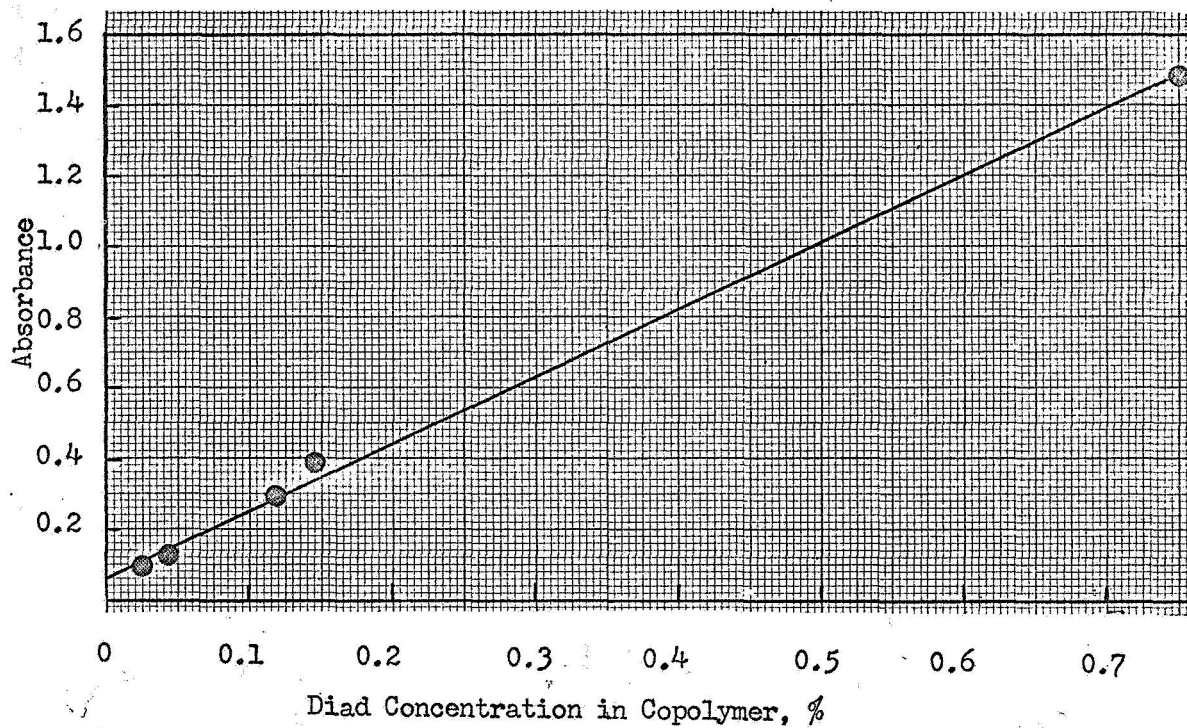0.16 r_2 = 1.43.

Fig. 5. Relation between the DCPA diad concentration in
the copolymer and the absorbance at 368 mμ for 0.1%
solutions.